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AN INVESTIGATION OF THE FIRST ROW TRANSITION-METAL FLUORIDE MOLECULES

USING ESR SPECTROSCOPY

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ABSTRACT

The ground state electronic configuration and magnetic parameters
have been determined for several first row transition metal mono-,
di-, and tri-fluoride molecules from their ESR spectra at $4^\circ K$. The
molecules studied have high spin electronic configurations with less
than 5% of the free electron spin density residing on the fluorine(s),
indicative of highly ionic bonding. Theory and experiment have been
correlated to establish or predict their ground electronic states and
geometries.

Introduction

The bond energy relationships for the metal fluoride molecules have been discussed by Hildenbrand,[1] and references are also to be found there to mass spectrometric studies of the species vaporizing from the solid fluorides, or from the solid fluorides plus the elemental metals. Although many transition-metal mono-, di-, and trifluorides have been observed in some spectroscopic manner, an understanding of their electronic properties is far from complete. Most of the monofluorides have been observed spectroscopically and characterized in the gas-phase,[2] but the lowest state has often not been ascertained (e.g., TiF, VF, NiF). Hastie, et al,[3,4] have measured the IR spectra of the difluorides in matrices, assigned vibrational frequencies, and deduced or estimated bond angles. However, other than TiF_2[5] and CuF_2,[6] which have been observed via ESR, the ground states of the difluorides are unknown. Those authors have also observed ScF_3[7] and TiF_3[8] in the IR and concluded that ScF_3 is planar (D_{3h}) but that the planarity of TiF_3 was less certain.

Relevant data on transition-metal di- and tri-halides other than fluorides has been given by Thompson and Carlson[9] and discussed in a review by Gruen.[10]

Theory has lagged considerably behind experiment. Besnainou and Whitten have recently calculated the ground state of NiF_2 to have a bond angle of 162° and the Ni-F bond to be slightly covalent.[11] Yates and Pitzer have recently made an _ab initio_ study of the trifluorides.[12] All are planar high-spin molecules except CrF_3 which is 10° out-of-plane. MnF_3 is found to be $^5E'$ and should therefore exhibit Jahn-Teller instability.

Much of the ESR work that we discuss here is incomplete in that more thorough studies in both neon and argon matrices are needed. Also, we have not hesitated to predict the ground state properties of species on the basis of the known properties of the transition-metal ions in these highly ionic fluorides or from the known properties of isoelectronic molecules.

Molecular Ground States

Figure 1 is a summary of the present state of knowledge of the ground states of the first-row transition-metal mono-, di-, and trifluorides. The states underlined are uncertain or predicted. The trifluoride data in row four are taken from the recent calculations of Yates and Pitzer.[12]

ScF_n. ScF has been thoroughly studied experimentally[2,13] and theoretically.[14] Optical spectroscopy in matrices at $4^{\circ}K$[13] proved that its ground state is $(\sigma^2)^1\Sigma$ rather than $(\sigma\delta)^3\Delta$ as in isoelectronic TiO.[15] The IR spectrum of ScF_2 indicates that it is bent with an estimated bond angle of 135°; its electronic ground state is not

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known. Knight and Wise, in very recent unpublished work,[16] have seen the ESR spectrum of ScF_2 which appears near $g = 2$ as an octet of triplets. The octet splitting, about 80G arises from ^{45}Sc ($I = 7/2$) and the triplets, 10-12 G splitting, are due to the two equivalent fluorine atoms. Further analysis is needed to establish whether it is linear or bent. Theory[12] predicts that ScF_3 is planar with a $^1A_1'$ ground state. The planar structure is in agreement with the IR results of Hastie, et al.[7]

TiF_n. TiF is isoelectronic with VO and is therefore expected to have a $(\sigma\delta^2)^4\Sigma$ ground state,[17,2] and the observed optical transitions in the gas phase do involve a lower $^4\Sigma$ state.[18] However, in recent ESR work at 4°K in our laboratory, the spectrum of TiF was not observed, suggesting either that TiF was not being produced and trapped at 4°K or that the ground state is not $^4\Sigma$. Since many experiments were run, possibly producing TiF in several ways, it is probable that the latter is the case, so that the most likely alternative ground state, $(\sigma^2\delta)^2\Delta$, is indicated in Fig. 1.

TiF_2 has been established to be bent by both IR[4] and ESR[5] studies. The latter have shown it to have a $^3B_1$ ground state with the unpaired electrons in d orbitals perpendicular to the plane of the molecule. These spins do not produce any observable fluorine hyperfine splitting so that it is inferred that $A_\perp(F)$ and $A_{||}(F)$ are $<\sim25$ MHz.

TiF_3 is planar with the one unpaired electron in a $4s_s + 3d_{z^2}$ hybrid orbital perpendicular to the plane of the molecule.[5] IR spectra[8] are in accord with this. The fluorine hyperfine splittings are observed as $|A_{||}| = 12$ and $|A_\perp| = 48$ MHz.

VF_n. Investigation of these molecules is in progress, and only the ESR lines shown in Fig. 2 have been observed after the vaporization of solid VF_3 and trapping in argon at 4°K. A strong perpendicular line at $g = 3.92$ is observed split by ^{51}V ($I = 7/2$) hyperfine interaction. Each line can be resolved into a 1:2:1 triplet arising from the hyperfine splitting of two equivalent fluorine atoms as shown in the lower part of Fig. 2. Although one cannot be positive, the absence of further structure indicates that the molecule is linear. We cannot, however, definitely rule out the angle of 150° estimated from IR spectra.[4] If linear, the molecule has a $^4\Sigma$ ground state, as does VO (if bent, the ground state would probably be $d^3(b_1''a_1'a_2'')$ $^4B_1$). The measured magnetic parameters are, assuming $g_\perp = 2.00$, $A_\perp(^{51}V) = 581(3)$ MHz, $A_{||}(^{51}V) = 205(20)$ MHz, $A_\perp(F) = 28.6(9)$ MHz, $|D| \gtrsim 0.48$ cm^{-1}.

VF, isoelectronic to CrO, is indicated to have a $(\sigma\delta^2\pi)$ $^5\Pi$ ground state, which could then not be observed in matrix ESR spectra. VF_3 should be a planar $^3A_2'$ molecule according to Yates and Pitzer,[12] and this should be easily proved if and when it is matrix-isolated.

CrF_n. The top of Fig. 3 shows a perpendicular ESR line at about $g =$ 6 attributed to CrF indicating that it has a $^6\Sigma$ ground state, which is compatible with the gas-phase optical spectrum.[19] As Fig. 3 shows, the shape of the line in neon and argon matrices is quite different. The molecule appears to be in more than one site in argon and is partially oriented in both matrices.[6,20] ^{53}Cr (I = 3/2, 9.5% natural abundance) hfs may be observable on the neon line where it yields $|A_\perp(Cr)| = 36$ MHz. The fluorine hfs is again smaller than the linewidth, i.e. <~20 MHz. A high field xy line should also appear if the molecule is $^6\Sigma$, and in argon one is observed at 5203 G. From the 1144 and 5203 G lines in argon, assuming $g_{||} = 2.002$, one can calculate $g_\perp = 1.989$ and $|D| = 0.56$ cm^{-1}, where the uncertainty may be 10%.

CrF_2 has not been clearly identified in these spectra. A line at 2648 G in argon is also observed in neon and can be attributed to a $^5\Sigma$ molecule; however, it does not appear to be reproducible. The absence of a CrF_2 ESR spectrum can be accounted for by assuming that it is linear and has an orbitally-degenerate ground state, such as $^5\Pi_g$.

CrF_3 has been clearly identified by the xy line near $g = 4$ shown at the bottom of Fig. 3. Three equivalent fluorine atoms give four hf lines, in this case 35 MHz apart. It is not possible to definitely say whether the molecule is planar so that we cannot establish whether the slightly pyramidal $^4A_2$ ground state proposed by Yates and Pitzer[12] is correct. From the line position at $g^e = 3.950$, assuming that $g_\perp \lesssim g_e$, one finds that $|D| \geqslant 0.59$ cm^{-1}.

MnF_n. Recently completed ESR work on MnF and MnF_2 shows unequivocally that their ground states are $^7\Sigma$ and $^6\Sigma_g$, respectively.[21] Small but resolved fluorine hfs is observed for both molecules in addition to the Mn (I = 5/2) splittings. The zero-field splitting is quite different in the two molecules: $D = -0.0107$ cm^{-1} in MnF and ± 0.37 cm^{-1} in MnF_2. MnF_3 has not been observed but is predicted to be planar with X^5E'.[12]

FeF_n. Investigation of these molecules is incomplete at present. FeF_2 and FeF_3 appear to have been observed in the ESR. Two weak xy lines, each with a possible hf triplet splitting of 38 G, are observed at 1531 and 2445 G. They indicate that FeF_2 is probably linear (in agreement with the IR spectrum[4]) with a $^5\Sigma_g$ ground state. The FeF_3 line is very clear as a quartet at $g \cong 6$, as shown in Fig. 4 where it is compared with the CrF_3 line. The F hfs is about twice that in the chromium trifluoride. The lack of additional splittings indicates that FeF_3 is planar and therefore has a $^6A_1'$ ground state, in agreement with theory.[12] From the effective $g^e = 5.960$, assuming $g_\perp \lesssim g_e$, one finds $|D| \geqslant 0.84$ cm^{-1}.

FeF has not been observed in the ESR implying either that it has not been isolated or that its ground state is not $^6\Sigma$.

CoF_n and NiF_n. Only nickel fluoride has been attempted using both photolysis and vaporization of solid NiF_2. In neither case was a reproducible spectrum observed. Since NiF_2 molecules should have been trapped from the vaporized solid,[22] it suggests that the molecule is linear but with a degenerate ground state. However, since this result apparently disagrees with the structure deduced from IR spectra[4] ($\theta = 165 \pm 8°$) and computed using non-empirical SCF calculations,[11] more work is needed to establish the (audaciously) assigned $^3\Pi$ state given in Fig. 1.

CuF_n. CuF has been observed in the gas-phase[23] and the $^1\Sigma$ ground state appears to be well established. The ESR spectrum of CuF_2 shows clearly that it has a $^2\Sigma$ ground state.[6] The g tensor components depart considerably from g_e and the fluorine hfs is larger than any of the other transition-metal fluorides: $A_\perp = 206$, $A_{||} = 308$ MHz. CuF_3 has not been detected spectroscopically.

Discussion

A general observation for all of the fluoride molecules studied via ESR is that the fluorine hyperfine splitting is very small and not resolved in some cases. This, coupled with the fact that the ^{19}F nucleus has a large magnetic moment, indicates that the unpaired spins in these molecules are essentially confined to the metal atoms. This means that they are in metal non-bonding orbitals even when a $3d\sigma$ or $4s\sigma$ orbital is available for bonding to the ligands. The implication is that the molecules are all highly ionic and are best considered as M^+F^-, $M^{+2}(F^-)_2$, and $M^{+3}(F^-)_3$. It is then to be expected, and is observed as shown in Fig. 5, that as one proceeds across the Periodic Table the F hfs will increase, since the ionization potentials of the metals increase. ($A_\perp(F)$ is plotted there since it was the only splitting observed for most fluorides. Generally $A_{||}(F)$ will be larger than $A_\perp(F)$.)

Monofluorides.

If these molecules are looked upon as M^+F^- then their ground states and optical spectra should reflect the properties of the M^+ ion. The ground-state configuration of the gas-phase M^+ ions are given in Fig. 1 and indicate that in Ti^+, Mn^+, and Fe^+ the 4s level is low enough to be occupied. Then we will speculate on two approximate rules for forming the configurations and ground states of these fluorides:

Let $\sigma(4s + \lambda 3d_{z^2}) = \sigma$ and $\sigma(3d_{z^2} - \lambda' 4s) = \sigma'$, where λ and λ' are constants less than unity,

1. If M^+(gas) has a ground-state configuration involving 4s then σ is effectively stabilized in the fluoride molecule and σ^2 can occur.

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2. d orbitals in the molecules fill up in the order δd, πd, $\sigma d(=\sigma')$ with the highest spin possible.

These rules work well for ScF through CrF. For both MnF and FeF, where $3d^n 4s$ is the lowest configuration of the metal ion, it is assumed that the $\sigma' \cong 3d_{z^2}$ orbital is also lower and is occupied to give the highest possible spin. In CoF, NiF and CuF where the 4s orbital lies increasingly higher, we assume the σ' orbital also lies higher. (Note that the ground states chosen here for CoF and NiF differ from the less ionic CoH and NiH which are $\sigma^2\delta^3\pi^3$, $^3\phi$ and $\sigma^2\delta^3\pi^4$, $^2\Delta$, respectively.[2])

These two rules then account for our choice of ground states for MF molecules in Fig. 1, and it remains to be seen whether we have chosen correctly. It is clear from a comparison of these states with the closely related MO molecules that in almost all cases low-lying excited states occur which are probably almost as important thermodynamically as the ground state.

Unfortunately only CrF and MnF have been observed in the ESR. The most striking difference between them is their zero-field-splitting parameters which are ± 0.56 and $- 0.01$ cm^{-1}, respectively. (The value for MnF is essentially the same in sign and magnitude as MnH.[24]) Theory must be applied to explain that difference.[25]

Difluorides

The infrared work of Hastie, et al[4] indicates that ScF_2 and TiF_2 are strongly bent, CrF_2 and FeF_2 are linear, and NiF_2 and CuF_2 are bent at an angle of $165 \pm 8^\circ$. VF_2, MnF_2, and CoF_2 are estimated to have angles of 150°, 180°, and 170°, respectively. We will propose here that all molecules to the right of VF_2 are linear and that VF_2 is uncertain but may be slightly bent. Since the larger angles ($>165^\circ$) determined by Hastie, et al, are the most uncertain then this proposal does not really depart significantly from their findings.

If the metal atoms in these molecules may be considered as essentially M^{+2} ions then their lowest states involve 3d and 4s orbitals (not 4p). The Walsh diagram for BAB molecules must then be altered to consider predominantly d electrons on A rather than p electrons. This was done earlier by Hayes[26] and Weltner and McLeod[27] and has been discussed in a recent review.[28] 16 of the 18 valence electrons of TiF_2 fill up levels favoring a bent molecule and the remaining two go essentially into non-bonding d orbitals on titanium perpendicular to the plane of the molecule, resulting in a triplet ground state (see Fig. 1).[5] However, addition of further electrons to give high spin states places them in higher-lying antibonding levels, as Hayes has indicated in explaining the linearity of MnF_2.[21] Although VF_2 may still be bent, it seems likely that the remainder of these difluorides are linear, particularly when it is known that MnF_2 [21,26,4,28] and CuF_2 [6,4] are linear.

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NiF_2 is somewhat controversial. Büchler, et al,[29] from molecular beam experiments, found no dipole moment and therefore supported a linear structure. Milligan, et al,[30] Hastie, et al,[4] and Van Leirsburg and DeKock,[31] from IR matrix studies, place the angle at 180°, 165 ± 8°, and 152°, respectively. A recent Hartree-Fock SCF calculation[11] yields an angle of 162°. However, from the reasoning leading to the assignments in Figure 1, a linear $^3\Pi$, or possibly $^3\Phi$, ground state seems most likely.

There may be a trend in the zero-field-splitting parameters, $|D|$, in going across the Periodic Table. Ti, V, Mn, and Fe difluorides have $|D|$ = 0.0782, > 0.48, 0.37, and 0.16 cm^{-1}, respectively, in approximate accord with increasing and then decreasing multiplicities.

Trifluorides

There appears to be complete agreement between Yates and Pitzer's[12] calculated ground states and those of the three molecules observed via ESR, within the rather restricted information that the experiments supply. The multiplicities agree and all molecules appear to be planar (D_{3h}) or the departure from planarity is small. The predicted small non-planarity of CrF_3[12] cannot be resolved by its ESR spectrum (Figs. 2 and 3).

The theory indicates very small spin densities on the F atoms, as observed. In the one case where complete data could be obtained from the ESR, i.e. TiF_3, there is a discrepancy between calculated and observed spin distributions on Ti. Theory indicates about 94% $3d_{z^2}$ character whereas experiment indicates only about 30%. While part of this discrepancy may also reside in the approximate procedure used in the derivation of the experimental value from the ESR data, it is likely that the theoretical calculation tends to underestimate the 4s contribution to the wavefunction.

Conclusion

Although many of the molecular states given in Fig. 1 are uncertain, the general scheme is supported by ESR data and is not in grave opposition to other experimental work. The molecules are clearly very ionic and the spins are almost entirely localized on the metal ion.

Among the diatomics, even though the ground states of isoelectronic species are not the same, it is clear that the same low-lying states will occur in each (e.g., ScF and TiO) and will be the thermodynamically important ones in both cases.

A transition-metal difluoride and its corresponding oxide often have the same ground state and can be expected to have the same group of low-lying states. A good example is FeO and FeF_2 where the low-lying states in both cases are presumably $^7\Sigma$, $^5\Sigma$, and $^5\Delta$. The ground

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state of FeO has only recently been settled to be $^5\Delta$ [32] and for some time it was thought to be $^7\Sigma$ or $^5\Sigma$.[33,34] Then FeF_2 is similar but with some transposition of the lower states.

Yates and Pitzer's[12] calculations for the trifluorides have provided a good basis for understanding this series, and experiment seems to support their theory.

There are many gaps to be filled in Fig. 1 and a need to push on to the second and third rows of the Periodic Table in making correlations.

Acknowledgments

Addenda:

Dr. G. Rosenblatt has pointed out a reference to ScF_3 that we missed: E.W. Kaiser, W.E. Falconer, and W. Klemperer, J. Chem. Phys. 56, 5393 (1972). Those authors show by electric deflection measurements that ScF_3 is pyramidal, in contrast with the theory and IR results mentioned above.

Figure 1 shows VF_2 as bent, but the latest spectrum in Fig. 2 indicates that it is probably linear.

References

1. D.L. Hildenbrand, Adv. High Temp. Chem. 1, 193 (1967).

2. Spectroscopic Data Relative to Diatomic Molecules, edited by B. Rosen (Pergamon Press, Oxford, 1970).

3. J.W. Hastie, R.H. Hauge, and J.L. Margrave, High Temp. Science, 1, 76 (1969).

4. J.W. Hastie, R.H. Hauge, and J.L. Margrave, Chem. Comm., 1452 (1969).

5. T.C. DeVore and W. Weltner, Jr., J. Am. Chem. Soc. 99, 4700 (1977).

6. P.H. Kasai, E.B. Whipple, and W. Weltner, Jr., J. Chem. Phys. 44, 2581 (1966).

7. R.H. Hauge, J.W. Hastie, and J.L. Margrave, J. Less-Common Metals, 23, 359 (1971).

8. J.W. Hastie, R.H. Hauge, and J.L. Margrave, J. Chem. Phys. 51, 2648 (1969).

9. K.R. Thompson and K.D. Carlson, J. Chem. Phys. 49, 4379 (1968).

10. D.M. Gruen, Progr. Inorg. Chem. 14, 119 (1971).

11. S. Besnainou and J.L. Whitten, paper given in 32nd Symposium on Molecular Spectroscopy, Columbus, Ohio, TH 1, June 14, 1977.

12. J.H. Yates and R.M. Pitzer, J. Chem. Phys. (to be published).

13. D. McLeod, Jr. and W. Weltner, Jr., J. Phys. Chem. 70, 3293 (1966).

14. P.R. Scott and W.G. Richards, Specialist Periodical Reports (The Chemical Society, London), Molecular Spectroscopy 4, 70 (1976).

15. W. Weltner, Jr. and D. McLeod, Jr., J. Phys. Chem. 69, 3488 (1965).

16. L.B. Knight, Jr. and M. Wise (private communication).

17. P. Kasai, J. Chem. Phys. 49, 4979 (1968).

18. R.L. Diebner and J.G. Kay, J. Chem. Phys. 51, 3547 (1969).

19. B. Kleman and U. Uhler, Can. J. Phys. 37, 537 (1959).

20. W. Weltner, Jr., Adv. High Temp. Chem. 2, 85 (1969).

21. T.C. DeVore, R.J. Van Zee, and W. Weltner, Jr. (to be published).

22. T.C. Ehlert, R.A. Kent, and J.L. Margrave, J. Am. Chem. Soc., 86, 5093 (1964).

23. R. Ritschl, Z. Phys. 42, 172 (1927); L.H. Woods, Phys. Rev. 64, 259 (1943).

24. See W. Hayes, P.D. McCarvill and T.E. Nevin, Proc. Phys. Soc. A70, 904 (1957 and references given there.

25. See A. Carrington and A.D. McLachlan, Introduction to Magnetic Resonance (Harper and Row, N.Y., 1967) pages 158-162.

26. E.F. Hayes, J. Phys. Chem. 70, 3740 (1966).

27. W. Weltner, Jr. and D. McLeod, Jr., J. Chem. Phys. 42, 882 (1965).

28. W. Weltner, Jr., submitted to Berichte der Bunsengesellschaft.

29. A. Büchler, J.L. Stauffer, and W. Klemperer, J. Chem. Phys. 40, 3471 (1964).

30. D.E. Milligan, M.E. Jacox, and J.D. McKinley, J. Chem. Phys. 42, 902 (1965).

31. D.A. Van Leirsburg and C.W. DeKock, J. Phys. Chem. 78, 134 (1974).

32. P.C. Engelking and W.C. Lineberger, J. Chem. Phys. 66, 5054 (1977).

33. R.F. Barrow and M. Senior, Nature (London) 223, 1359 (1969); J.B. West and H.P. Broida, J. Chem. Phys. 62, 2566 (1975).

34. P.S. Bagus and J.H.T. Preston, J. Chem. Phys. 59, 2986 (1973).

Fig. 1

M⁺ ION	3d4s	3d²4s	3d⁴	3d⁵	3d⁵4s	3d⁶4s	3d⁷	3d⁸	3d⁹
MF	ScF	TiF	VF	CrF	MnF	FeF	CoF	NiF	CuF
MO (ISOELECTR TO MF)	TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO	ZnO
MF₂	ScF₂	TiF₂	VF₂	CrF₂	MnF₂	FeF₂	CoF₂	NiF₂	CuF₂
MF₃	ScF₃	TiF₃	VF₃	CrF₃	MnF₃	FeF₃	CoF₃	NiF₃	CuF₃

GROUND STATES (ESTABLISHED AND PREDICTED) OF TRANSITION-METAL FLUORIDES

Underlined States Are Predicted

$^{51}VF_2 / AR$

1708 G (g* = 4)

500 G

1704 G

20 G
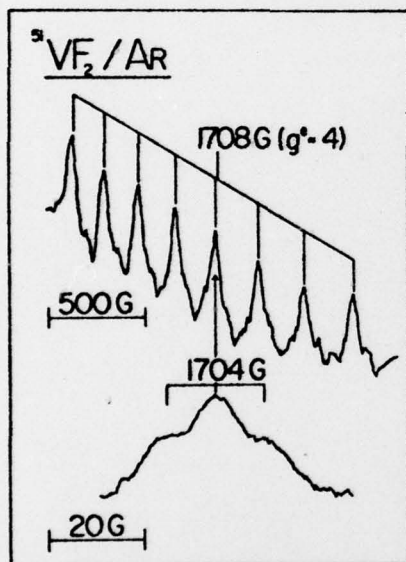
Fig. 2. ESR spectrum of VF_2 molecule trapped in an argon matrix.

ARGON 1144 G   CrF   NEON 1137 G ^{53}Cr hfs

$\theta = 0°$ $\theta = 90°$

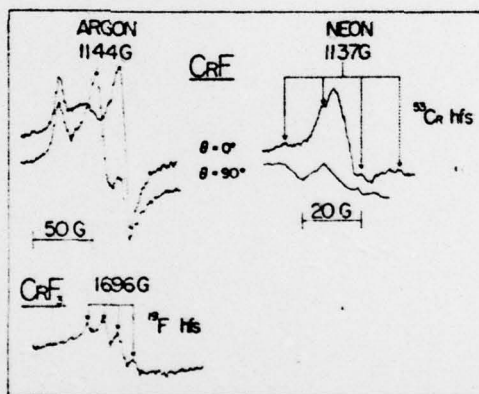50 G   20 G

CrF₃   1696 G ^{19}F hfs

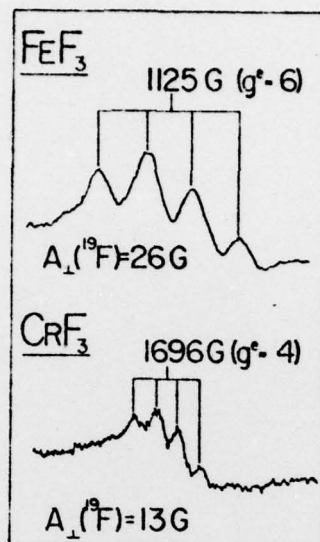Fig. 3. ESR spectra of CrF molecule in argon and neon matrices and CrF_3 molecule in an argon matrix.

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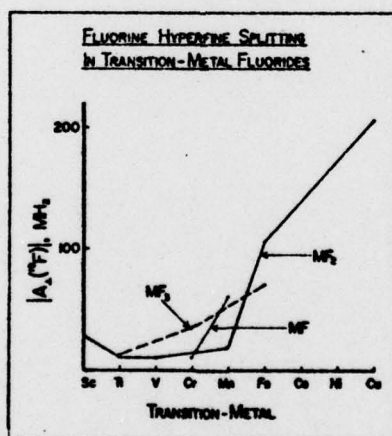Fig. 4. ESR spectra of FeF₃ and CrF₃ molecules trapped in argon matrices.

Fig. 5